

Not for Publication

Presented Before the Division of Gas and Fuel Chemistry
American Chemical Society
Boston, Massachusetts, Meeting, April 5-10, 1959

The Surface Properties of the
Quinoline-Insoluble Fraction of Pitch

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Introduction

The general consensus of the literature on binder materials for the production of Soderberg electrodes in the aluminum industry is that a coal-tar pitch is the preferred binder material.¹⁾ Studies directed toward establishing the most suitable methods for the preparation of an electrode-binder pitch from a coal tar and methods for improving the binding quality of pitches have been of considerable interest to both the producer and the consumer of electrode-binder pitch. Although compressive-strength measurement on test electrodes has been a satisfactory method of evaluating pitches for production of carbon electrodes, this method is time-consuming. It would be much more satisfactory to be able to predict electrode-binder efficacy on the basis of the chemical and physical properties of the pitch. Only then would it be possible to interpret the binding action in terms of pitch composition and perhaps to modify the pitch in a manner which would have a predictable effect on the binder action.

Charette and Bischofberger²⁾ concluded that pitch quality, as expressed by the compressive strength of test electrodes, is apparently not a function of any pitch property taken individually, but rather of a combination of properties. These investigators and others have considered correlations of compressive strength of electrodes with such properties of pitch as coking value, density, aromaticity, softening points, and distribution of fractions produced by solvent extraction.

One general method of characterizing pitches is that of solvent analysis. In one such technique, the pitch is extracted first with a paraffinic solvent and the residue is then re-extracted successively with benzene and quinoline. Martin and Nelson³⁾ state that "in pitch binder quality, the quinoline-insoluble (Q.I.) fraction, essentially a nonfusible powder, is important".

The technological importance of the Q.I. fraction of pitch is recognized by the inclusion of a Q.I. minimum in many specifications for electrode-binder pitches. Information on the scientific significance of the Q.I. material is rather scarce. It is known that the Q.I. material per se does not contribute directly to the binding action of the pitch,⁴⁾ and generally it is considered as inert material which may have a beneficial effect in decreasing the effect of temperature on the viscosity of pitch.⁵⁾ Thus, one notes in the literature a tendency to consider the Q.I. portion of pitch as a finely dispersed carbonaceous filler of questionable function in the binding action of the pitch.

Because little information could be found on the surface properties of the Q.I. fraction of pitch and because studies of the surface chemistry of carbon black have led to a better understanding of the use of this material in the rubber industry, an exploratory study of the surface properties of the Q.I. portion of pitch was made. It was hoped that this information might lead to a better understanding of the function of Q.I. material in the applications of pitch as an electrode binder.

Experimental

For this work, a total of nine experimental binder pitches, representing a considerable range of Q.I. content, was selected. The usual analytical data on these pitches are summarized in Table I. Pitches 1 through 6, representing a range of Q.I. from 2.44 to 13.1 per cent, had been prepared to an approximate constant softening point of 90°C. In order to achieve rather extreme variation in Q.I. content, pitch A was thermally treated to produce pitch B having a very high benzene-insoluble and quinoline-insoluble content. Pitch C was produced to have a low Q.I. content by centrifugation of a quinoline suspension of the parent tar of pitch A, followed by removal of the quinoline and further distillation.

Table I

Analytical Data on Experimental Pitches

Pitch	Softening Point, °C C.I.A.*	Benzene Insoluble, Wt %	Quinoline Insoluble, Wt %	Beta- Resin**	Coking Value, Wt %	Carbon, %	Hydrogen, %	Atomic C/H Ratio
1	89.0	33.2	13.1	20.1	56.8	93.34	4.36	1.80
2	90.2	32.6	12.8	19.8	57.1	93.41	4.07	1.93
3	93.5	29.7	10.58	19.1	54.1	93.31	4.18	1.87
4	94.9	28.0	9.13	18.9	52.7	92.88	4.44	1.76
5	90.6	17.5	6.87	10.6	50.2	92.55	4.38	1.78
6	88.2	13.0	2.44	10.6	49.8	91.35	4.77	1.61
A	102.3	25.5	12.4	13.1	56.7	93.22	4.24	1.84
B	98.5	50.3	35.0	15.3	64.9	93.48	4.00	1.96
C	95.0	25.0	4.2	20.8	51.9	93.29	4.52	1.73

* Cube-in-Air Method.

** Benzene Insoluble Minus Q.I. Equals Beta-Resin.

- 1 Thermal Treatment of a 74°C pitch at 380°C for 24 hours and back-blending with 9.1 per cent of starting pitch.
- 2 Laboratory distillation of soft pitch from a production tar.
- 3 Laboratory distillation of 36.2 weight per cent from a production tar.
- 4 Blend of 88.55 weight per cent 105°C pitch (produced by distillation of light tar at 50 mm to 300°C) with 11.45 per cent of coal-tar distillate oil (boiling 230-270°C).
- 5 A production pitch after removal of n-heptane solubles.
- 6 Laboratory distillation of a 69°C pitch from light tar.
- A A pitch produced by plant distillation of production tar.
- B A pitch produced by thermal treatment of pitch A to have maximum benzene-insoluble and quinoline-insoluble content.
- C A pitch produced by adding quinoline to the parent tar of pitch A, centrifuging this mixture to remove insolubles, and then distilling.

The Q.I. fractions used for the present study were isolated as follows:
A 100 g portion of pitch was crushed and ground to pass a 60-mesh sieve. The pitch was then added slowly with stirring to 250 ml of warm (70-90°C) quinoline in a 600 ml beaker. After 15-20 minutes at this temperature, the mixture was filtered through a

Buchner funnel fitted with a Whatman No. 50 filter paper. The retained Q.I. were washed with an additional 250 ml of warm quinoline in small portions and then with 500 ml of benzene to remove the quinoline. After air drying, the Q.I. were oven-dried at 110-115°C for one hour. This method of preparation gave yields of Q.I. materials nearly equal to those obtained by the analytical procedure and reported in Table I.

Surface-area measurements were made using the method of Brunauer, Emmett, and Teller.⁶⁾ The samples were degassed at 200°C for 12 hours before measuring the nitrogen isotherm at 77°K.

Specimen electrodes were prepared using the various pitches as binders according to the procedure of Jones, Simon, and Wilt.⁷⁾

Results and Discussion

The data on the Q.I. fractions of the experimental pitches are summarized in Table II. For these particular samples, it was noted that the surface area per gram of Q.I. tends to decrease as the amount of Q.I. in the pitch increases (Figure 1). This trend is exhibited both by pitches 1 through 6 and by the interrelated series, A, B, C, although the rate of change varies. This observation suggests that a process such as thermal treatment, which tends to increase the amount of Q.I. in the pitch, also produces an agglomeration or increase in particle size of the Q.I. material.

Table II

Data on the Quinoline Insolubles

Quinoline- Insoluble Fraction	C.V. - Q.I. Q.I.	Surface Area, m ² /g	Surface Area per 100 g Pitch, m ²	Carbon, %	Hydrogen, %	Atomic C/H Ratio
1	3.34	9.4	123	92.59	3.06	2.54
2	3.46	10.4	133	93.02	2.43	3.21
3	4.1	13.2	140	93.06	2.01	3.89
4	4.8	16.3	148	91.60	2.11	3.64
5	6.28	16.8	116	93.13	2.00	3.90
6	19.4	22.9	55	91.45	2.47	3.10
A	3.57	15.9	197	94.76	1.89	4.21
B	0.85	8.0	280	94.67	3.04	2.61
C	11.4	19.4	82	93.36	2.30	3.41

It is of interest to note that thermal treatment of a pitch (A) containing 12.4 per cent Q.I. with a surface of 15.9 m²/g yielded a product pitch (B) containing 35.0 per cent Q.I., but with a surface of only 8.0 m²/g. When the Q.I. content was reduced to 4.2 per cent by extraction of the parent tar with quinoline, centrifugation to remove most of the Q.I., removal of solvent, and distillation, the residual Q.I. in the pitch (C) had a surface area of 19.4 m²/g.

In a number of cases (such as the Q.I. from pitches 6 and 2), the Q.I. was found to be almost entirely spherical in habit (Figures 2 and 3). It will be noted that the particle sizes are of the same order of magnitude as those anticipated from surface area measurements, with pitch 6 having the smaller particle size and higher surface area.

Having shown that Q.I. material can differ in surface area and particle size, it was of interest to examine the surface for differences in chemical reactivity. For this purpose, the polarographic reducibility of the surface of the Q.I. material was determined by the method of Hallum and Drushel.⁸⁾ As noted in Figure 4, the polarographic reducibility of the Q.I. appeared to be a direct function of the surface

area. This relationship between polarographic reducibility and surface area was taken as an indication of the chemical uniformity of the surface of the Q.I. material. The limited number of samples examined prohibit any firm position on this indication. However, the significance of surface reducibility might be more profitably pursued in the study of Q.I.'s of the same surface area where differences in reactivity are suspected. A sample of petroleum coke of comparable surface area showed no reducibility.

Before considering the effect of the surface area of the Q.I. portion of pitches on the properties of electrodes prepared from pitches, the available data were examined for evidence of surface effects during the coking of the pitch itself. If the surface area of the Q.I. is an important factor in binding action, it seemed reasonable to anticipate some effect on the yield of coke available from the pitch.

If it is assumed that all quinoline-soluble material is available for the formation of coke and that Q.I. is relatively unchanged during coking, a plot of coke formed (coking value - Q.I.) per unit weight of Q.I. versus the surface area per unit weight of Q.I. should give an indication of the effect of Q.I. surface area on the yield of coke. Figure 5 shows this relationship and indicates that Q.I.'s with a high surface area promote a high yield of coke per unit weight of Q.I. The variant pitches B and C, produced from A, show this same qualitative relationship. This relationship suggests that the surface of the Q.I. may function as the site of coke formation.

The usual test data for the specimen electrodes are tabulated in Table III. The apparent density, resistivity, and compressive strength of the electrodes as a function of the amount of surface available from the Q.I. in 100 g of binder are shown in Figures 6, 7, and 8. These figures show that apparent density and compressive strength reach a maximum at about 125-150 m² of surface in 100 g of pitch, and the resistivity reaches a minimum in the same region.

Table III
Test Data on Specimen Electrodes
Prepared from Experimental Pitches

<u>Pitch</u>	<u>Apparent Density,</u> <u>g/cm³</u>	<u>Resistivity,</u> <u>ohm-cm</u>	<u>Compressive Strength,</u> <u>kg/cm²</u>
1	1.46	60.1 x 10 ⁻⁴	557
2	1.47	60.3 "	577
3	1.44	65.2 "	472
4	1.45	59.0 "	541
5	1.43	66.8 "	468
6	1.39	70.1 "	357
A	1.45	59.6 "	490
B	1.36	74.0 "	356
C	1.46	55.5 "	538

Also, these figures suggest that an optimum surface area or particle size of Q.I. exists which permits the formation of electrodes with optimum properties. The results are quite similar to those of Krylov, et al, who found in their studies of the free-carbon content of pitch that at about 16 per cent free carbon the density and compressive strength of electrodes pass through a maximum and resistivity reaches a minimum.⁹⁾

Conclusions

Although the Q.I. fraction of an electrode-binder pitch reportedly has no binding action in itself, it is credited with being important to electrode-binder

efficacy of the pitch. The actual role of the Q.I., however, remains vague. It was therefore the purpose of this study to examine the surface properties of Q.I.'s of several experimental pitches in the hope that some information might thus be obtained which would be helpful in elucidating the role of the Q.I. On the basis of nine different pitches, the Q.I.'s of which varied, irregularly, from 2.44 to 35 per cent, the following effects were observed:

1. The larger the percentage of Q.I. content of a pitch, the smaller is the surface area per gram of Q.I., and hence the larger is the average particle size. This is qualitatively borne out by electron photomicroscopy.
2. The polarographic reducibility of the Q.I. appears to be directly related to surface area, an indication that the reactivity of the surface is essentially uniform.
3. The yield of new coking value per gram of Q.I., $\frac{C.V. - Q.I.}{Q.I.}$, is directly related to the surface area per gram of Q.I. This suggests that the Q.I. surface may serve as the site of new coke formation.
4. Evaluation of test electrodes prepared from these pitches indicates that there may be an optimum range of interfacial area between the Q.I. and the remainder of the pitch. In this range, the apparent density and compressive strength of the electrodes pass through a maximum and the resistivity through a minimum.

This study has been an examination of some of the parameters of the Q.I. which might shed light on its function in the pitch. It is hoped that these preliminary, generalized trends of some Q.I. properties will be useful to investigators who are currently exploring this field.

Acknowledgment

This work was done by the Coal Chemicals Project sustained by the United States Steel Corporation. The authors wish to express their appreciation to the Corporation's Applied Research Laboratory for permission to use some of the data presented herewith. The contribution of the Institute's Research Services Department is also gratefully acknowledged.

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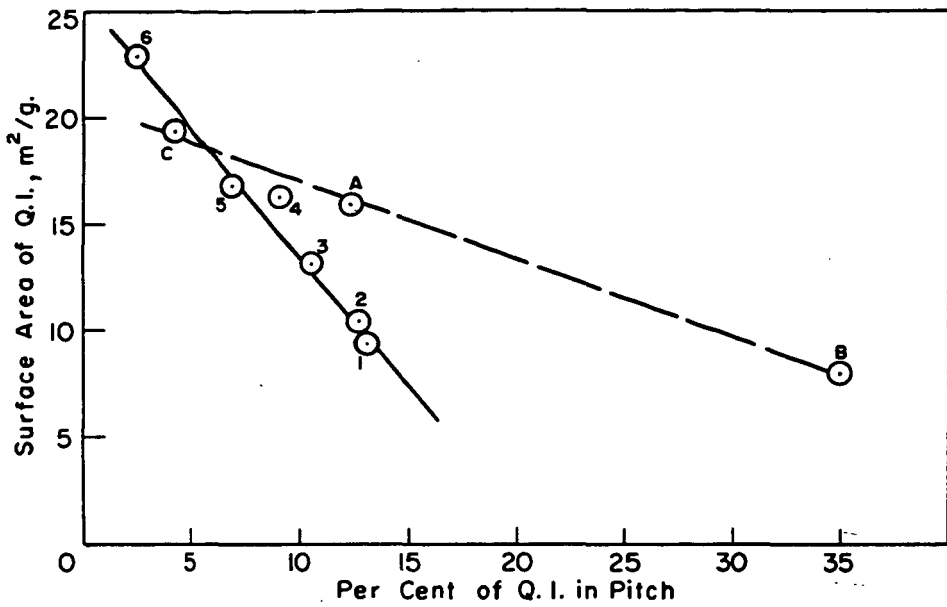


Figure 1. The Q.I. Content of the Pitch Versus Q.I. Surface Area

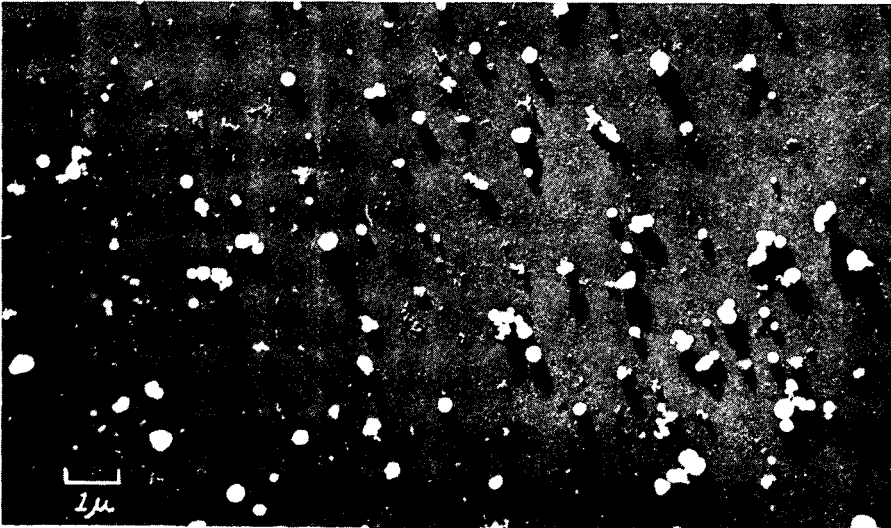


Figure 2. Photomicrograph of the Q.I. of Pitch 6, Illustrating a Q.I. of High Surface Area

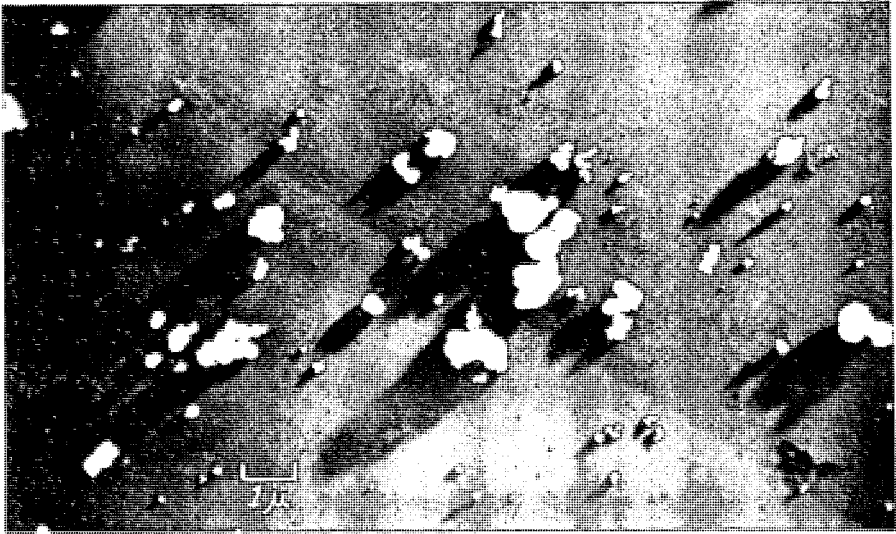


Figure 3. Photomicrograph of the Q.I. of Pitch 2, Illustrating a Q.I. of Low Surface Area

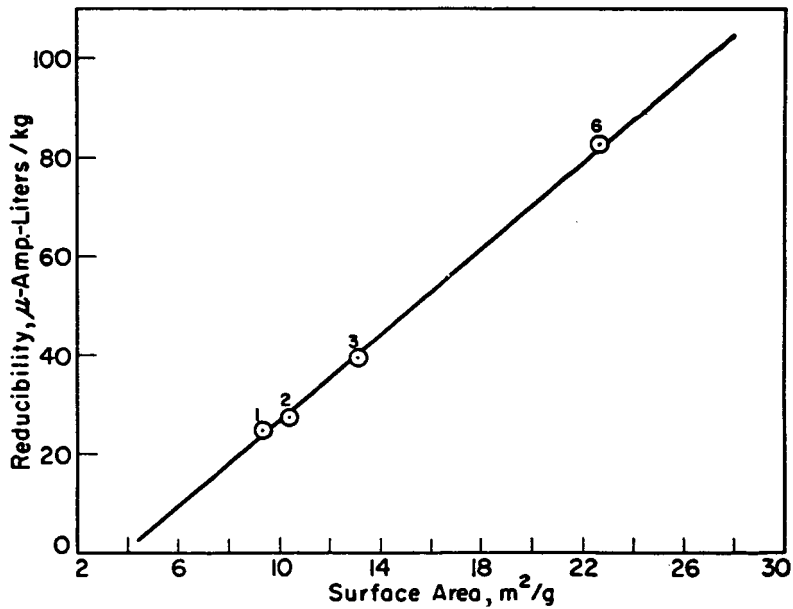


Figure 4. Relationship of the Polarographic Reducibility to the Surface Area of the Q.I.

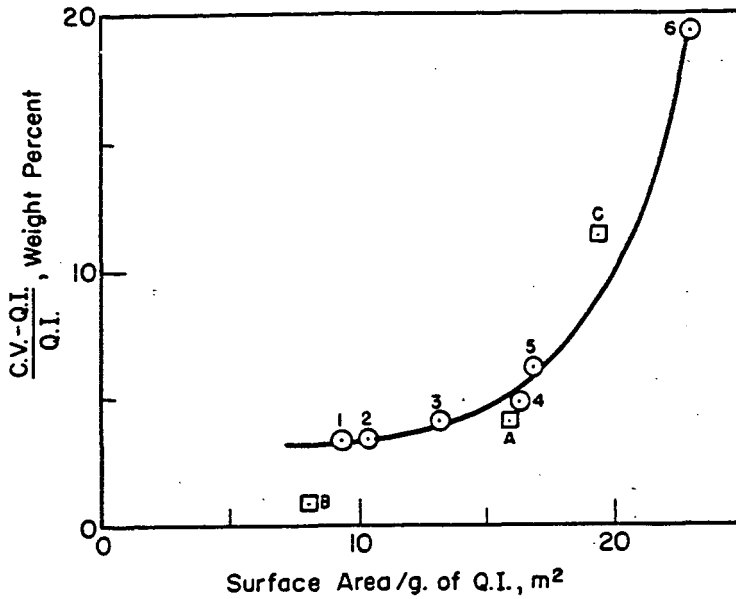


Figure 5. Relationship Between the Yield of New Coking Value per Gram of Q.I. (C.V. - Q.I./Q.I.) and the Surface Area per Gram of the Q.I.

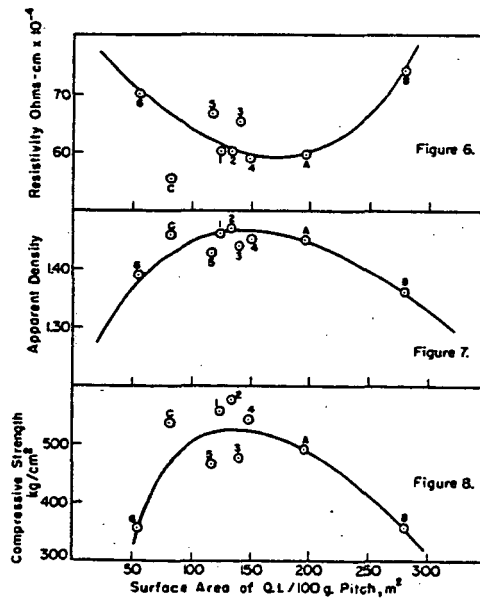


Figure 6, 7, & 8. Relationships Between the Resistivity, Apparent Density, and Compressive Strength of Test Electrodes Prepared from Each of the Experimental Pitches and the Surface Area of the Q.I. in 100 g of the Respective Pitch